Liquid Crystals 'Made of Gold'

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The simple linear coordination of gold(I) helps in the understanding of structure-property relationships in liquid crystals based on metal-containing molecules. This simple geometry also allows the preparation of materials showing a range of mesophases, based on both rod-like and disc-like molecules.

A SHORT INTRODUCTION TO LIQUID CRYSTALS

Most solid materials produce isotropic liquids directly upon melting. However in some cases one or more intermediate phases are formed (called mesophases), where the material has some ordered structure but has already the mobility characteristic of a liquid. These materials are thermotropic liquid crystals (or mesogens) and can display several transition temperatures between phases: crystal-crystal transitions (as normal solids), melting point (solid to first mesophase transition), mesophase-mesophase transitions (when several mesophases exist) and clearing point (last mesophase to isotropic liquid transition) (1). Often the transitions are observed both upon heating and cooling (enantiotropic transitions), but sometimes they appear only upon cooling (monotropic transitions). A similar behaviour can occur upon destruction of the crystalline network by adding some solvent. These mesogens are called lyotropic liquid crystals and show temperature and concentration dependent mesophases. We will focus on the former, as lyotropic behaviour of gold compounds, although to be expected, has not been reported so far.

Liquid crystal behaviour is a genuine supramolecular phenomenon based on the existence of extended weak interactions (dipole-dipole, dispersion forces) between molecules. For these to be important enough it is usually necessary that the molecules have anisotropic shapes able to pack efficiently, so that these weak interactions can be high in number, co-operate, and become so strong as to keep the molecules associated in a preferred orientation, but free to move as they are not connected by rigid bonds. Most usually the molecules are rod-like (giving calamitic phases), or disc-like (giving columnar mesophases). The different mesophases are related to differently ordered molecular arrangements and are associated with characteristic textures when viewed in a microscope between crossed polarizers. Optical microscopy is a main technique for identification of the type of mesophase, but unequivocal identification sometimes requires low angle X-ray diffraction studies on the mesophase (preferably oriented). Differential Scanning Calorimetry (DSC) is also used in order to measure transition temperatures and enthalpies The molecular arrangements responsible for the main phases observed in gold-based mesogens are depicted in Figure 1, each rod or disc representing a molecule.

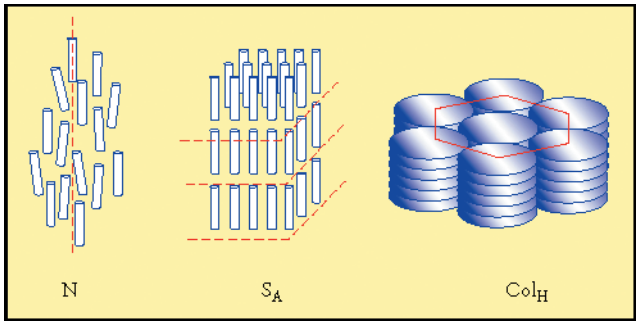


Figure 1 *Schematic representation of the molecular arrangements in nematic (N), smectic A (S_A) and columnar hexagonal (Col_H) mesophases.*

WHY GOLD?

Mesogenic behaviour was discovered in 1888 in organic molecules (2). Since then the structural

features favouring the appearance of organic mesogens have been reasonably well established. Usually rod-like molecules consist of a rigid core (two or more conjugated rings) associated with alkyl- or alkoxy-chains contributing to the polarizability of the molecule. The use of an extended conjugated core is a common strategy in order to increase the otherwise rather weak intermolecular interactions in organic molecules (hence their low melting points). Terminal groups introducing dipole moments (C≡N, halogen) are also common, as well as systems introducing hydrogen bonding interactions. Disc-like molecules are usually built around aromatic cores (Figure 2).

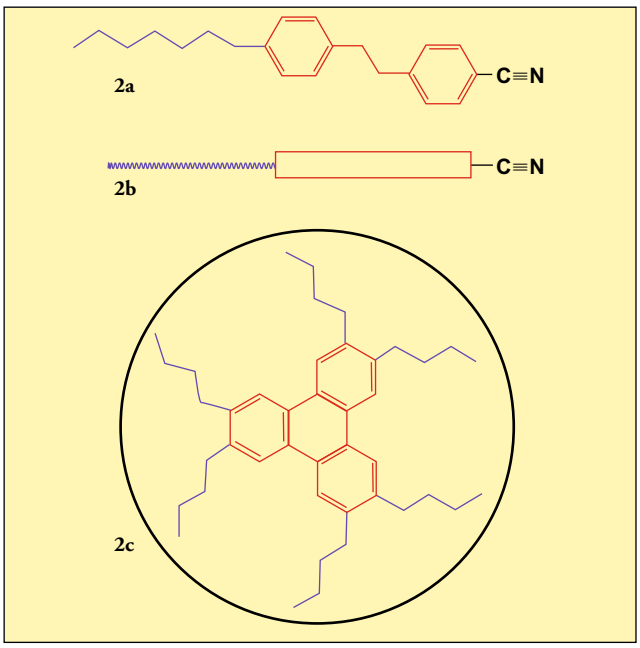


Figure 2 *A typical rod-like mesogenic molecule (***2a***) along with a schematic representation of the same molecule (***2b***), and a disc-like molecule based on a polyaromatic core (***2c***).*

Metallomesogens (mesogens based on metal-containing molecules) are much younger than organic liquid crystals. Their more systematic study began in the middle 80's (3). Soon it became apparent that, when a metal is involved, the transition temperatures of the materials are quite high. On the other hand, liquid crystals could sometimes be produced with molecules having bizarre shapes, for which no mesogenic behaviour would be expected in organic systems. Furthermore, the initial naïve ideas on the importance of the coordination geometry in determining the shape of the molecule (*eg* linear for rod shaped, square-planar for disc shaped), have made room for the evidence that bulky coordinated organic ligands very often disguise the initial geometry around the metal and determine the real shape of the molecule.

The metal centres with coordination numbers higher than two have very complex multipolar structures and it is difficult to grasp the role of the metal and establish a simple model that explains the so called 'structure-mesogenic behaviour relationship'. In these circumstances it is convenient to focus on the concept of linear coordination of gold(I) as the simplest model to try to identify the effect of the metal amongst other contributions. As a matter of fact, all the papers on gold-containing mesogens deal with gold(I), except for the case of the square-planar dithiobenzoate gold(III) complexes $[AuCl_2(S_2C\text{-}C_6H_4\text{-}OC_nH_{2n+1})]$ which gave S_A phases in the 150 – 200°C temperature range (4).

GOLD RODS: THE EFFECT OF THE METAL

Complexes of the type [XAuL] (X = halide) where L is a promesogenic ligand (*ie* a ligand having some properties favouring the appearance of mesomorphism, even if it is not liquid crystal itself) can be considered as compounds where XAu is a terminal group modifying the properties of L. Compared with other terminal groups, the presence of a metal produces dramatic effects. Thus the complexes $[XAuCN\text{-}C_6H_4\text{-}OC_nH_{2n+1})]$ give liquid crystals (smectic A phases, Figure 3) for X = Cl, Br but not for X = I (5). It is quite extraordinary that mesogens are obtained from molecules containing only one aryl ring and in fact the free isonitriles are not liquid crystals. With a biphenyl core the isonitriles are liquid crystals (nematic – or smetic A phases in the range 40-85°C), and the complexes $[XAuCN\text{-}C_6H_4\text{-}C_6H_4\text{-}OC_nH_{2n+1}]$ are liquid crystals (Figure 4) even for X = I (6). These results clearly illustrate the fact that the introduction of a metal dramatically increases the intermolecular interactions.

A closer look at the thermal behaviour of these two series of compounds (Figure 5) reveals very interesting features: For the phenyl isonitrile complexes (X-Ph-10) the melting and clearing points decrease in the order Cl > Br > I. This is also the variation of the clearing points for the biphenyl isonitrile compounds (X-biPh-10), but their melting points follow the opposite trend, I > Br > Cl. A simple explanation of this apparently contradictory behaviour can be given by considering

Figure 3 *Fan-shaped S_A texture of [ClAu($CNC_6H_4OC_6H_{13}$)] at 160°C upon cooling from the isotropic state (between crossed polarizers, x100).*

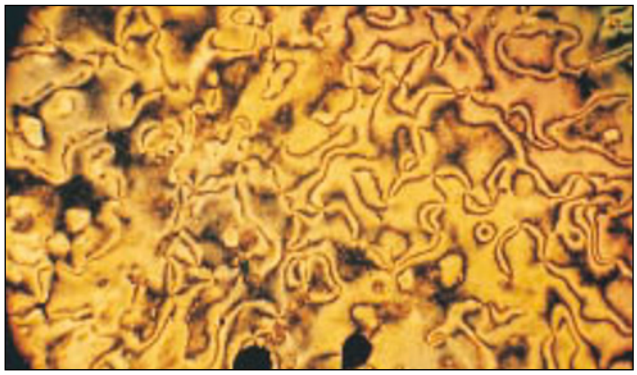


Figure 4 *Nematic schlieren texture of [ClAu($CNC_6H_4C_6H_4OC_4H_9$)] at 160°C upon heating from the solid state (between crossed polarizers, x100).*

two main contributions to the intermolecular interactions in condensed phases: a) the dipole moment associated with the X-Au bond; and b) the induced dipoles associated with the polarizability of the isonitrile. The variation in X-Au dipole moment is the same for the two series (Cl > Br > I), but the contribution of the isonitrile moiety can be very different. Compared with the polarizability of the phenyl isonitrile, that of the biphenyl can be much higher provided that the two aryl rings are coplanar, giving extended conjugation. This difference will be attenuated if the two aryls in the biphenyl unit are perpendicular and the conjugation is broken. On this basis the thermal properties observed can be explained as follows: the behaviour observed for the melting and clearing temperatures of the phenyl series indicates an important influence of the X-Au dipole, since both these transition temperatures increase with the value of this dipole. The clearing temperatures of the biphenyl systems follow the same trend, *ie* they behave as the phenyl system, and this suggests that in the mesophase the two aryl rings are not well conjugated; this is reasonable considering that in a fluid phase there is freedom for rotation around the aryl-aryl bond (Figure 5a). Finally, the melting points of the biphenyl system follow the trend opposite to that expected from X-Au dipole control. This suggests that in the solid state the biphenyl system has become coplanar producing a very polarizable molecule (Figure 5b). Moreover, the availability of electron density from the metal (higher for the less electronegative halogen, I > Br > Cl) controls the value of the induced dipole moments in the condensed state, and seems to be the dominant factor at this point, until the conjugation is broken upon melting.

Can this hypothesis be further supported? The answer is in Table 1 which indicates the lowest energy electronic transitions for the isonitriles and their complexes. This energy (K band) is a practical

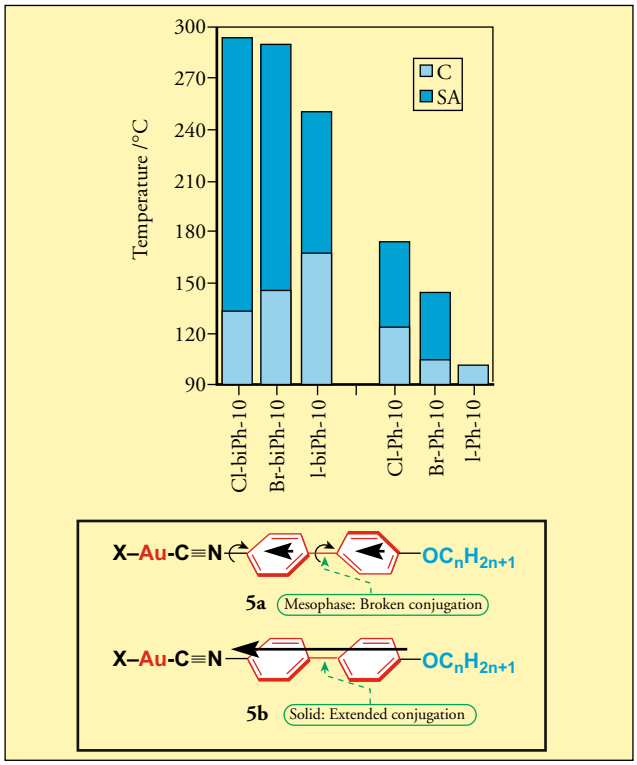
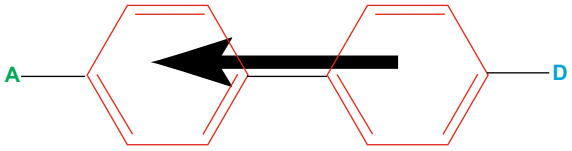


Figure 5 *Thermal properties of gold complexes with isonitriles having a phenyl or a biphenyl core, and proposed explanation for the different influence of the biphenyl core on the melting and the clearing points in compounds having a biphenyl core. The biphenyl moiety has less influence on the clearing point (a) than on the melting point (b) because its participation on the molecular polarization is much higher in the solid than in the mesophase.*

Table 1 *Relationship of the Visible K Band Energy with the Polarizability of the Molecule, its Variation from the Free Isonitriles to the Different Complexes, and the Variation in X-Au Dipolar Moment. A and D Stand for Acceptor and Donor Group, respectively.*

	A	Biphenyl E(cm^{-1})	polarizability	μ(Au-X)
Biphenyl	CN	34722	↓	↑ Cl, Br, I
	ClAuCN	32154		
	BrAuCN	32051		
	IAuCN	31847		
Phenyl	CN	40650		
	XAuCN	37037	(no variation for different X)	↑ Cl, I



The lower E, the higher the polarizability, the higher the induced dipolar moment, the higher the electrostatic interactions

measurement of the HOMO-LUMO separation and gives a very approximate idea of the polarizability of the molecule: The lower the energy of this band, the higher the polarizability of the molecule (7). It can be seen that: 1) The presence of the metal produces a dramatic increase in polarizability, as compared to the free isonitriles. 2) The change in halogen does not produce perceptible changes in polarizability in the case of phenyl isonitriles, hence the variations are not associated with this factor, but with variations in the X-Au dipolar moment. 3) The energy of the K band is sensitive to the halogen in the biphenyl systems, hence variations in polarizability are expected upon changing the halogen, in the order I > Br > Cl, as observed for the melting points.

The most important consequence of these observations is the realization that a strong increase in polarizability is introduced with the metal, associated with the high availability of electron density, as compared with the first and second row main group elements. Thus, in contrast with the usual practice when making organic liquid crystals, accumulation of conjugated aryl rings can lead to too strong intermolecular interactions when a transition metal is present, thus increasing the melting points to undesirably high values.

A number of mesogens have been described based on these [ClAuL] rod-like molecules. These include stilbazole (8), isonitrile (9), and carbene ligands (10, 11). It is interesting to note that the introduction of a lateral chain (Figure 6) produces an important decrease in the melting points of complexes 6b compared with 6a, as a consequence of diminished intermolecular interactions produced by the lateral substitution which, on an average, results in a larger distance between the dipoles in the molecules.

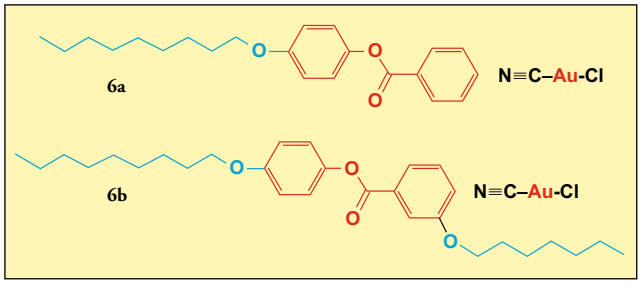


Figure 6 *Two gold mesogens structurally related, one having a lateral chain substituent.*

[(Alkynyl)Au(CNR)] complexes also give liquid crystals which are thermally unstable and usually decompose before or at the clearing temperatures (12, 13). This thermal lability is thought to be associated with the Au-(alkynyl) bond and makes these compounds undesirable for making liquid crystals, but might make them useful as precursors for gold deposition from an oriented fluid state.

When the alkynyl is replaced by fluorinated aryl rings (Faryl), which give more stable Au-Faryl bonds, thermally stable compounds are obtained (14). It is worth commenting on the behaviour of the large molecules containing two gold-isonitrile fragments linked by an octafluorobiphenyl group (Figure 7a),

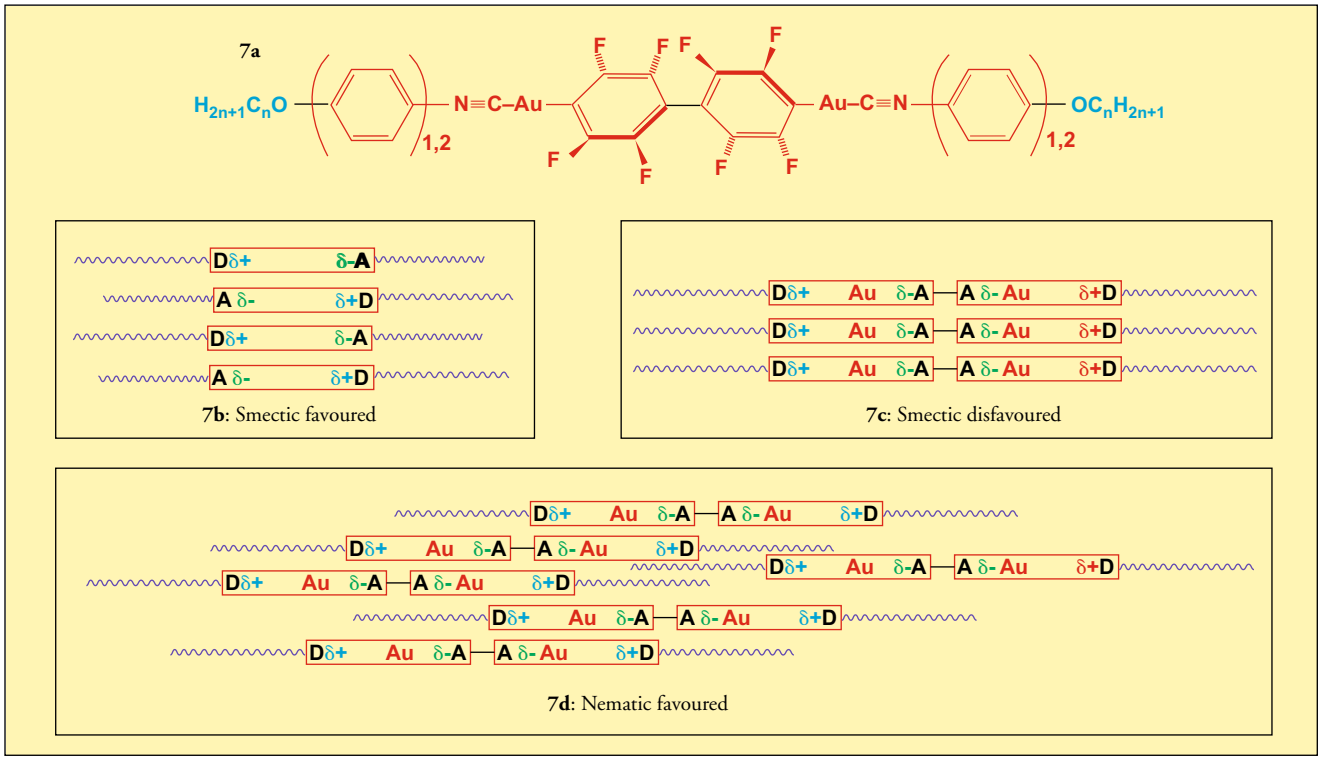


Figure 7 *A simple representation indicating how dipolar interactions can favour discrimination of aliphatic and aromatic areas (giving rise to smectic phases), or on the contrary its mixing (giving rise to nematic phases). A and D stand for Acceptor and Donor group, respectively.*

which give nematic phases in spite of their big molecular size. In effect, large organic molecules containing extended conjugated cores often display smectic phases because their interactions tend to associate the molecules defining aromatic and paraffinic areas, leading to a layer arrangement characteristic of the smectic phases (Figure 7b). The gold derivatives, being perfectly symmetric and highly polarizable, produce large local dipoles which lead to repulsive interactions if the molecules are packed in layers (Figure 7c), and favour arrangements where the aromatic and paraffinic areas are mixed, *ie*, where there is only orientational order as it occurs in the nematic phase (Figure 7d) (14).

Finally, the introduction of chiral centres might produce chiral phases. These have not been reported so far in the literature for gold mesogens, but recently in our laboratory we have found that the molecules sketched in Figure 8 do indeed produce chiral nematic (cholesteric, N*) mesophases (15). The texture of one of them is shown in Figure 9.

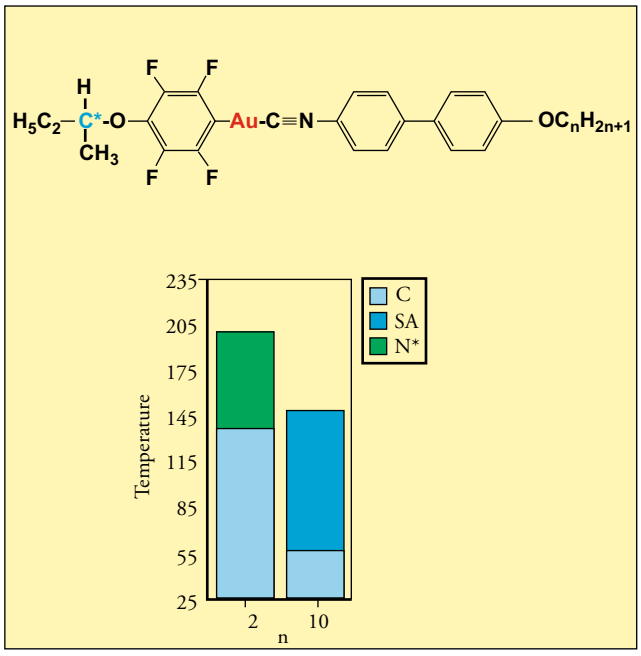


Figure 8 *Thermal properties of some gold chiral complexes. Amongst them a cholesteric phase is observed.*

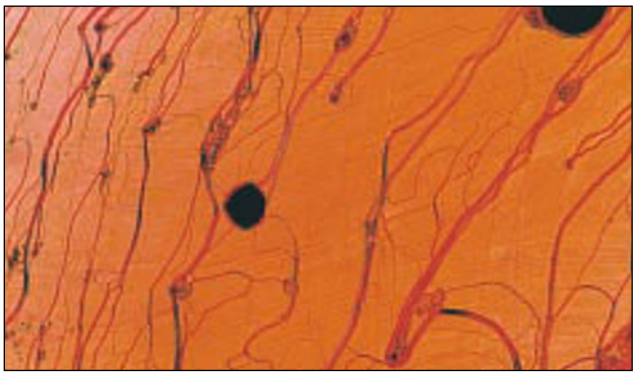


Figure 9 *Cholesteric phase of [((S)-EtMeCHOC$_6$F$_4$)Au(CNC$_6$H$_4$C$_6$H$_4$OEt)] at 152°C, upon heating (between crossed polarizers, x100).*

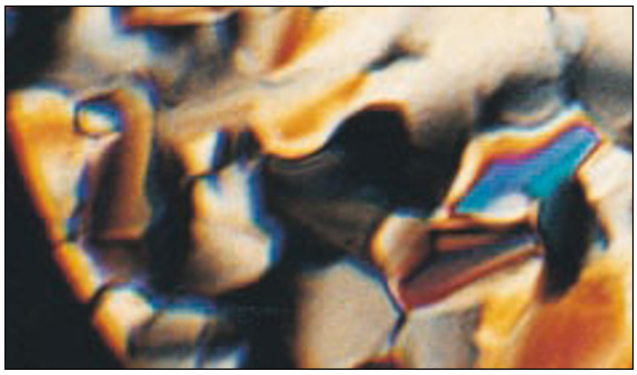


Figure 10 *Hexagonal columnar mesophase observed for [ClAu(CNC$_6$H$_2${OC$_6$H$_{13}$}$_3$] at 30°C (between crossed polarizers, x200).*

GOLD DISCS AND GOLD SANDWICHES: THE IMPORTANCE OF THE LIGAND

So far, the linear coordination of gold has given rise to rod-like molecules. It would appear that the metal coordination determines the bulk shape of the molecule. That it is not so is shown by the behaviour of the complexes [ClAu{CNC$_6$H$_2$-3,4,5-(OC$_n$H$_{2n+1}$)$_3$}] which (16), for alkoxy chains with six or more carbons, display columnar hexagonal mesophases at room temperature (Figure 10). This behaviour is typical of discotic molecules. These gold isonitrile molecules are not discotic when considered individually, but can produce a disc-like arrangement of paraffinic chains if they are considered by pairs in an antiparallel arrangement (Figure 11). In fact the X-ray results on the mesophase support this interpretation. Thus the columnar behaviour is a supramolecular property of the bulk material. In this interpretation it is not meant that there is any permanent association in pairs, just that each 0.4 nm thick disc in the column contains two molecules filling this space. It would be reasonable to think that this arrangement might be favoured by the aurophilicity phenomenon, but a similar behaviour is found for related compounds of Ni, Cu, Pd and Mo (17). This suggests that, even if aurophilicity could be operating in the solid state, it is unlikely to be important in the formation of thermotropic mesophases.

For the cation in the dicarbene complexes depicted in Figure 12a we might expect lath-like appearance under normal circumstances. But the very long chains attached to the nitrogen atoms are far from what is normal in other areas of chemistry, and the intra- and

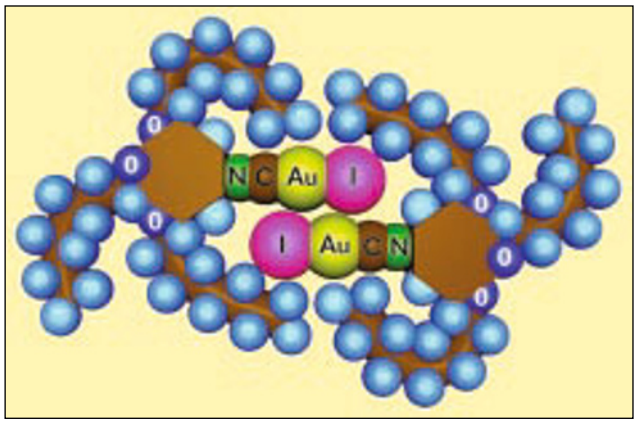


Figure 11 *Space-filling model showing how two semidiscotic molecules can give rise to a more or less discotic shape (according to x-ray studies on the mesophase).*

intermolecular interactions, as well as the anion-cation attractions lead to the cation structure 12b and bilayered arrangement 12c. The cations have interdigitated their chains, giving rise to paraffinic areas sandwiched between Au(bimy)$_2$ planes (bimy = 1,3-dialkylbenzimidazol-2-ylidene). The single crystal X-ray structure for the hexadecyl derivative shows that these bilayers of about 22 Å thickness are stacked to give a lamellar structure with a repeating spacing of about 26 Å. The anions (Br^-) and one water molecule per gold atom are located between the bilayers (18). It is likely that the molecular arrangement in the lamellar mesophase is related to that observed in the solid state.

These examples demonstrate that the ligand, and the neutral or ionic nature of the complexes have a determinant influence on the molecular shape and the best space filling arrangement, beyond the initial influence of the metal coordination.

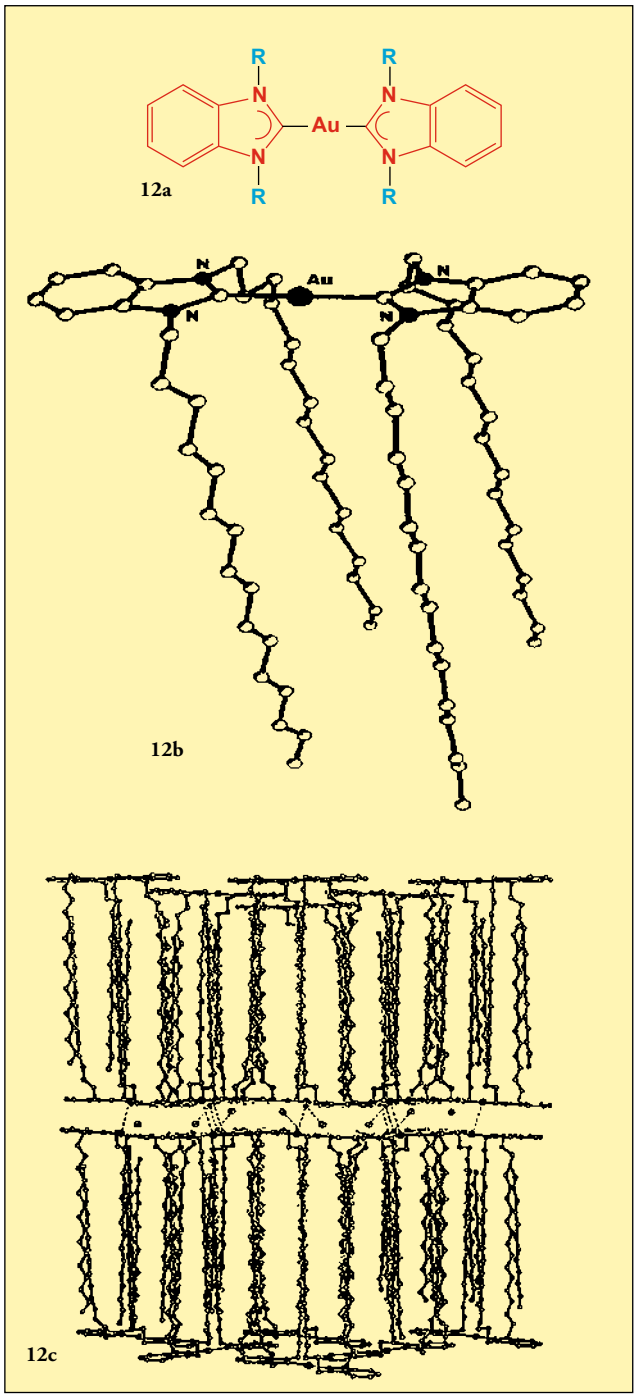


Figure 12 *Schematic formula (a), molecular single crystal X-ray diffraction structure (b), and solid state packing (c) of the cationic gold complex [Au{bimy($C_{16}H_{33}$)}$_2$]Br·H_2O (adapted from reference 18).*

CAN GOLD OFFER MORE FUN?: MAKING DISCS FROM RODS

It is known from long ago that gold pyrazolates have a trinuclear structure defining a basically hexagonal (or triangular) core (Figure 13a) (19). Conveniently substituted, this core is adequate for producing columnar organizations, which have been realized. Thus using bis-alkoxy or tris-alkoxy aryls in the positions R^1 and R^3, columnar hexagonal mesophases are obtained at temperatures not far from room temperature, although with a short range of mesomorphism (20).

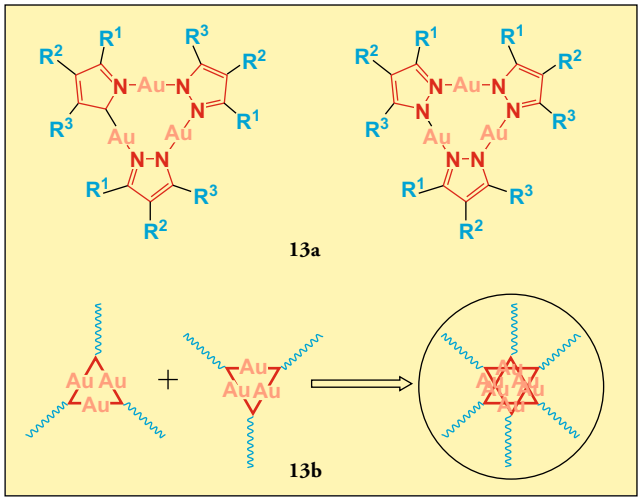


Figure 13 *Some gold pyrazolates giving rise to discotic shapes and columnar hexagonal mesophases.*

Less substituted systems also give rise to mesomorphism: Compounds with R^1 = R^3 = Me and R^2 = C_7H_{15}, C_8H_{17} also display columnar hexagonal mesophases, although in this case they are monotropic (obtained only on cooling the isotropic liquid obtained after melting). Again, the number of aliphatic chains per molecule is insufficient to fill a disc, but the molecules stacked in the alternate way shown in Figure 13b produce disc-like dimers (21).

These examples show that linear coordination, when associated with appropriate angled bidentate ligands, can also give rise to discotic nanostructures.

CONCLUSIONS AND PERSPECTIVES

In the modest number of papers on gold-containing liquid crystals which have been published to date it has

been proven that a careful choice of the ligands involved allows the preparation of thermally stable compounds, whereas others undergo easy decomposition. It is also clear that all kinds of mesophases can be produced based on linearly coordinated gold(I). The understanding of the structure-property relationships is also reasonably good, and these compounds have provided clues as to the role of the metal, which are also relevant to gaining a better understanding of the properties of other metallomesogens.

On this basis it would be interesting to explore some possibilities that can be envisaged. For instance the mesogenic organization might facilitate unidimensional conducting properties associated with gold-gold interactions, either in the mesophase or in glassy solid materials, retaining the mesophase organization. Discotic materials might produce wires based either on the mononuclear or the trinuclear systems just discussed. The probable miscibility of the gold mesogens with paraffin-rich organic polymers should be suitable for the homogeneous dispersion of gold in these media. Also, gold mesogens provide a viscous but fluid and easily processable source of gold, in which the molecules can be oriented at will. This might prove useful for processing and further easy deposition of gold metal in the electronics and decoration industries.

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ABOUT THE AUTHOR

Pablo Espinet is Professor of Inorganic Chemistry at the University of Valladolid (Spain). His main research interests are mechanistic aspects of catalytic and fluxional processes (mainly in palladium chemistry), and the making and tuning of metal-containing liquid crystals. It is in that later area that he is stimulated by the potential use of gold for the purposes reported in this review.

REFERENCES

1 The reader can find a comprehensive treatment on all aspects of Liquid Crystals in: 'Handbook of Liquid Crystals' ed. J.W. Goodby and G.W. Gray, VCH, Weinheim, 1999

2 F. Reinitzer, *Monatsch. Chem.*, 1888, **9**, 421

3 Metallomesogens. Synthesis, Properties and Applications', ed. J.L. Serrano, VCH, Weinheim, 1996

4a H. Adams, N.A. Bailey, D.W. Bruce, R. Dhillon, D.A. Dunmur, S.E. Hunt, E. Lalinde, A.A. Maggs, R. Orr, P. Styring, M.S. Wragg and P. M. Maitlis, *Polyhedron*, 1988, **7**, 1861

b P.M. Maitlis, D.W. Bruce, R. Dhillon, D.A. Dunmur, F.P. Fanizzi, S.E. Hunt, R. LeLaguedec, E. Lalinde, R. Orr, J.P. Rourke, N.J.S. Salt, J.P. Stacey and P. Styring, *New. J. Chem.*, 1990, **14**, 549

c H. Adams, A.C. Albéniz, N.A. Bailey, D.W. Bruce, A.S. Cherodian, R. Dhillon, D.A. Dunmur, P. Espinet, J.L. Feijoo, E. Lalinde, P.M. Maitlis, R.M. Richardson and G. Ungar, *J. Mater. Chem.*, 1991, **1**, 843

5 S. Coco, P. Espinet, S. Falagán and J.M. Martín-Alvarez, *New J. Chem.*, 1995, **19**, 959

6 M. Benouazzane, S. Coco, P. Espinet and J.M. Martín-Alvarez, *J. Mater. Chem.*, 1995, **5**, 441

7 M. Hedström, N.S. Benachenhou and J.L. Calais, *Mol. Eng.*, 1944, **3**, 329

8 D.W. Bruce, E. Lalinde, D.A. Dunmur and P. M. Maitlis, *Chem. Commun.*, 1986, 581

9 T. Kaharu, R. Ishii and S. Takahashi, *Chem. Commun.*, 1994, 1349

10 R. Ishii, T. Kaharu, N. Pirio, Sh.-W. Zhang and S. Takahashi, *Chem. Commun.*, 1995, 1215

11 Sh.-W. Zhang, R. Ishii and S. Takahashi, *Organometallics*, 1997, **16**, 20

12 P. Alejos, S. Coco and P. Espinet, *New J. Chem.*, 1995, **19**, 799

13 T. Kaharu R. Ishii, T. Adachi, T. Yoshida and S. Takahashi, *J. Mater. Chem.*, 1995, **5**, 687

14 For a more detailed discussion and the influence of the non-planarity of the -C_6F_4-C_6F_4 – bridge see: R. Bayón, S. Coco, P. Espinet, C. Fernández-Mayordomo and J.M. Martín-Alvarez, *Inorg. Chem.*, 1997, **36**, 2329

15 S. Coco and P. Espinet, results to be published.

16 S. Coco, P. Espinet, J.M. Martín-Alvarez and A.M. Levelut, *J. Mater. Chem.*, 1997, **7**, 19.

17a H. Zeng, C.K. Lai and T.M. Swager, *Chem. Mater.*, 1994, **6**, 101

b A.G. Serrette and T.M. Swager, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2342

18 K.M. Lee, C.K. Lee and I.J.B. Lin, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1850

19 G. Minghetti, G. Banditelli and F. Bonati, *Inorg. Chem.*, 1979, **18**, 658

20a J. Barberá, A. Elduque, R. Giménez, L.A. Oro and J.L. Serrano, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2832

b J. Barberá A. Elduque, R. Giménez, F.J. Lahoz, J.A. López, L.A. Oro and J.L. Serrano, *Inorg. Chem.*, 1998, **37**, 2960

21 S.J. Kim, S.H. Kang, K.-M. Park, H. Kim, W.-C. Zin, M.-G. Choi and K. Kim, *Chem. Mater.*, 1998, **10**, 1889